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UNITED STATES DEPARTMENT OF AGRICULTURE  
Agricultural Marketing Service  
Grain Division

Grain Moisture Determination

Karl Fischer Method

Apparatus:

1. Stein Mill equipped with condenser tube. (The condenser serves two purposes: (1) to condense the vapors during grinding, (2) as a means of adding methanol after the dry grind).
2. Dual automatic titration setups. Consists of reservoirs, burettes and drying tubes.
3. Electrometric titration setup. Any of the commercially available models can be used, or an arrangement as shown in Fig. 1 can be easily assembled. In this laboratory a circuit containing a 3-volt battery, toggle switch, 750,000 ohm resistor and a Weston Model 440 microammeter in series with the electrodes is used.
4. Hydrometer jars, 100 ml. One jar is needed for each titration carried out in any titration period.
5. Pan or cup to fit around Stein Mill cup.
6. Magnetic Stirrer.

Reagents:

1. Methyl Cellosolve, Purified or also known as Ethylene Glycol Monomethyl Ether, Purified (Fisher Scientific Co.)
2. Pyridine, A.C.S. Reagent Grade.
3. Sulfur Dioxide, Anhydrous.
4. Methanol, Absolute, Baker Analyzed Reagent.
5. Karl Fischer Reagent. (K.F.R.) - Available commercially or it can be prepared by the method of Peters and Jungnickel (3) as follows:



For each liter of solution to be made mix in a suitable size flask: 425 ml. of C. P. pyridine and 425 ml. of anhydrous Methyl Cellosolve. Tare the flask while stoppered. Add 98 g. of sulfur dioxide gas (or 70 ml. of liquid SO<sub>2</sub>) while the flask is immersed in an ice bath. Insert a plug of cotton in the neck of the flask surrounding the delivery tube and twirl or shake continuously during the addition. As the end of the addition is neared the solution takes on a somewhat yellowish color. The flask should be large enough so that, in the event an excess of sulfur dioxide is added, there will be room to add the calculated amounts of the other ingredients to bring the solution to the correct proportions. With the flask still immersed in ice water, add 133 g. of C. P. iodine slowly with shaking after each small addition.

6. Standard water-in-methanol solution. (S.W.S.). - This is prepared according to the method of Mitchell and Smith (2). One milliliter of the S.W.S. should contain approximately 5 mg. of water. It should be either discarded or restandardized at frequent intervals. It is prepared in the following manner. Pipet 5 ml. of water into a liter volumetric flask. Fill to the mark with methanol and mix thoroughly. Methanol from the same container must be used in standardizing the solutions.

Use the following procedure in the standardization. Transfer the solution to the S.W.S. burette reservoir. Add 50 ml. of methanol to the titration cell and titrate to end point. Then add 20 ml. of K.F.R. from the burette and titrate with S.W.S. to a new end point. Calculate the number of milliliters of K.F.R. required to react with 50 ml. of methanol and with 1 ml. of S.W.S. Duplicate titrations should check to 0.01 ml. The method of making the calculations is explained by using the following specific example. In a standardization it is found that 50 ml. of methanol reacts with 280 ml. K.F.R. and that 22.47 ml. of K.F.R. react with 21.20 ml. of S.W.S. Therefore:

$$1 \text{ ml. S.W.S. } \div \frac{22.47}{21.20} = 1.06 \text{ ml. K.F.R.}$$

$$\begin{aligned} \text{Milliliters of K.F.R. required to titrate 49.75 ml. methanol} \\ = \frac{49.75 \times 2.80}{50} = 2.79 \text{ ml.} \end{aligned}$$

(For practical purposes, 50 ml. S.W.S. contain 49.75 ml. of methanol and .25 ml. of water).

$$\begin{aligned} \text{Milliliters of K.F.R. required to titrate 50 ml. of S.W.S.} \\ = 50 \times 1.06 = 53.00 \text{ ml.} \end{aligned}$$

Milliliters of water added to 50 ml. of S.W.S = .25 ml.

Milliliters of H.F.R. required to titrate 1 g. of water  

$$= \frac{53.00 - 2.79}{.25} = 200.84 \text{ ml.}$$

Water in 50 ml. S.W.S =  $\frac{53.00}{200.84} = .2639 \text{ g.}$

Water in 1 ml. S.W.S =  $\frac{.2639}{1} = .0053 \text{ g.}$

1 ml. H.F.R.  $\frac{.0053}{1.06} = .0050 \text{ g. H}_2\text{O}$

In this laboratory it has been found more convenient to prepare standard water solution in one-liter quantities. This amount lasted about 2 weeks and did not have to be restandardized during that time. In case it is desired to prepare a large volume which would require restandardization at intervals, the following method of restandardization could be followed. Titrate a known weight of sodium tartrate, dihydrate, (1) with H.F.R. Calculate the titer of the H.F.R. from the known water content of the salt. Then titrate the S.W.S. with H.F.R. and calculate its water concentration.

#### Procedure:

Weigh 10 g. of grain with an accuracy of  $\pm .005 \text{ g.}$  Grind in the Stein Mill for at least 3 minutes. Add 200 ml. of methanol through the condenser tube and grind for 5 minutes more. Cool the cup by immersion in a pan of cold water without detaching the cup from the mill. Remove cup from mill and immediately decant into an hydrometer jar, stopper and allow to stand until suspended matter has settled to the bottom (5 to 15 minutes depending on the material tested). Pipet a 20-ml. aliquot into the titration cell, add 40 ml. of methanol, and titrate.

Carry out the dead stop back titration procedure (4, 5) in the following manner. With the magnetic stirrer in operation and the switch in the electric circuit to "on," add H.F.R. from the burette until the electric current reaches its maximum value and does not recede when addition of H.F.R. is discontinued. Add S.W.S. drop by drop until the current decreases.

Blank determinations on the methanol should be made at each titration period. Titrate 50 ml. of methanol in the usual way and calculate the milliliters of H.F.R. required to react with 60 ml. of methanol (the volume used in the determination).



In the grinding process sufficient heat is generated to make the brass parts of the mill and the copper condenser act as catalysts for the oxidation of some of the methanol with the production of formaldehyde and water. It is, therefore, necessary to run a blank titration on the solvent after it has been used in the mill for the same length of time as the grinding of the sample. This blank is constant and, once it is established, its determination need not be repeated before each titration period.

Since the K.F.R. deteriorates slowly, it is necessary to determine its titer each time it is used.

The calculations involved in a titration are explained by means of the following specific example. In a certain moisture determination on a sample of grain the following data applied:

1 ml. S.W.S.  $\pm$  1.06 ml. K.F.R.

1 ml. K.F.R.  $\pm$  .0050 g. H<sub>2</sub>O

60 ml. methanol  $\pm$  3.00 ml. K.F.R.

Constant correction 0.20% H<sub>2</sub>O

20.00 ml. K.F.R. used in direct titration

0.16 ml. S.W.S. used in back titration

Percent of water =  $\left[ .0050 (20.00 - 3.00 - 0.16 \times 1.06) \right] \times 100 - .20 = 8.2$

#### Literature Cited

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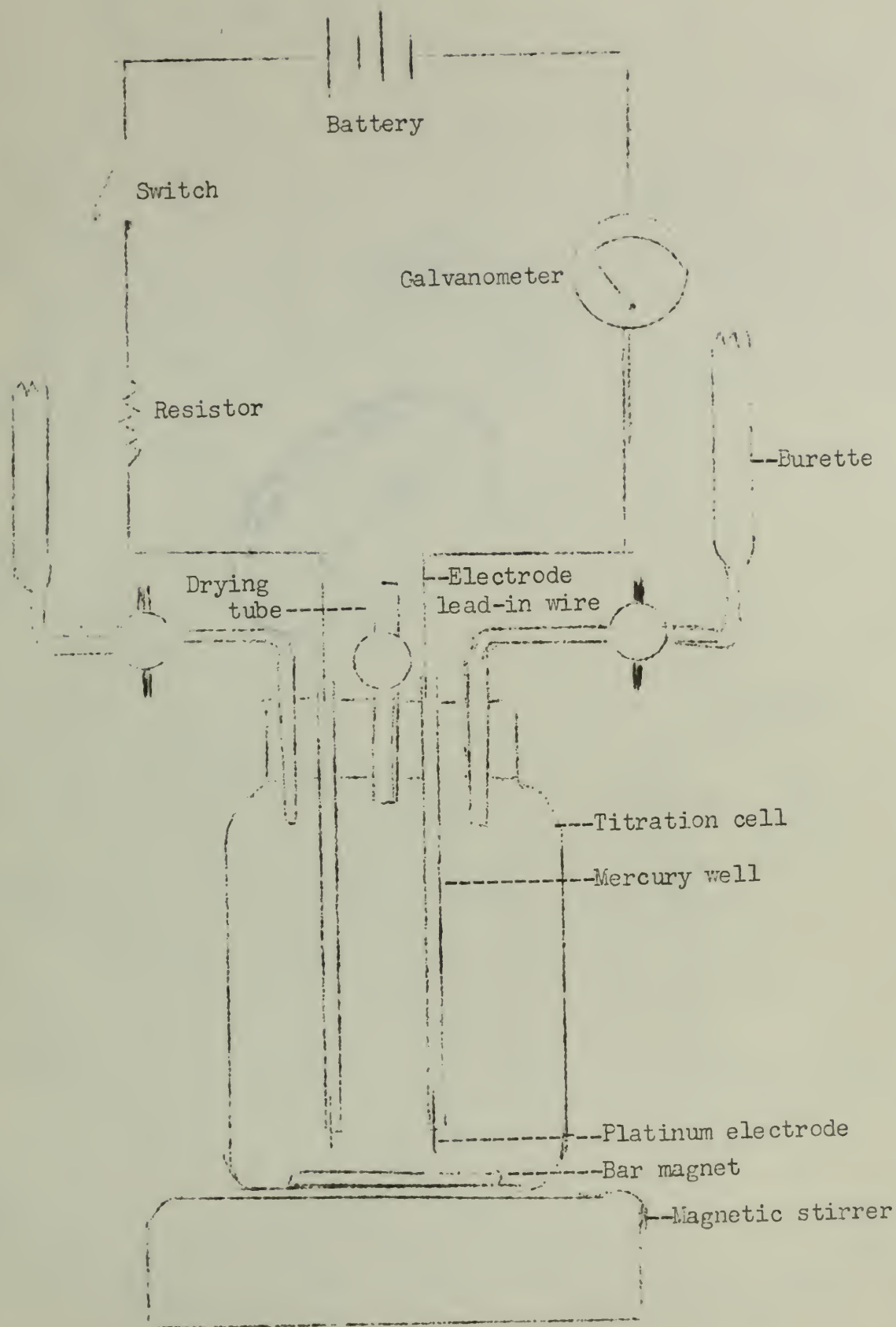


Figure 1. Schematic Drawing of Titration Assembly

